On the computation of the entropy in the microcanonical ensemble for mean-field-like systems

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Abstract

Two recently proposed expressions for the computation of the entropy in the microcanonical ensemble are compared, and their equivalence is proved. These expressions are valid for a certain class of statistical mechanics systems, that can be called mean-field-like systems. Among these, this work considers only the systems with the most usual hamiltonian structure, given by a kinetic energy term plus interaction terms depending only on the configurational coordinates.

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The microcanonical ensemble generally is not the chosen ensemble for the computation of thermodynamic observables of statistical systems. Exact or approximate analytical procedures are usually easier in the canonical ensemble. However, a recent surge of interest for the statistical properties of systems with “unconventional” thermodynamics has made desirable to perform calculations in both ensembles. These systems are characterized by the fact that they are small [1], and thus surface effects cannot be neglected, or by the long range nature of the interaction between their microscopic constituents [2]. In both cases additivity of the energy and of other thermodynamic functions does not hold.

The most relevant feature of long range systems is that very often, even in the thermodynamic limit, canonical and microcanonical ensembles are not equivalent, and this justifies the necessity to perform calculations in both ensembles: contrary to the usual case, the system can have different values of the macroscopic observables, if it is considered at fixed energy or at fixed temperature. The issue of ensemble inequivalence, first discussed theoretically by Hertel and Thirring [3], has later been thoroughly treated in the mathematical physics literature (see Refs. [4, 5] and references therein). The inequivalence has been put in evidence both in self-gravitating systems [6, 7, 8] and in other, magnetic-type, systems [9, 10, 11], which are often easier to study. A fundamental tool for the mathematical analysis of ensemble inequivalence has been found in the theory of large deviations [12], as applied to statistical mechanics (see Ref. [13] and references therein): this application employs the important concept of macrostates of the systems [4, 14, 15].

In simple terms, nonequivalence can be ascribed to the nonconcavities that are found in the microcanonical entropy [4]. Not only does this lead to different results for the entropy, if computed in the microcanonical and in the canonical ensembles, but it can also be the cause, in the microcanonical ensemble, of negative specific heats [6, 7, 8, 9, 11, 16, 17, 18]. It has also been found that ensemble inequivalence is associated to the presence of first order phase transitions in the canonical ensemble [7, 9].

Through the use of large deviation techniques, it is possible to derive a general expression for the microcanonical entropy of statistical mechanics systems belonging to a certain class [4, 10, 13], that we can call mean-field-like systems. This terminology is motivated by the observation that in these systems the interactions can be thought of as giving rise to a mean field acting on the particles, although this may not be easily visible as in, e.g., some simple lattice magnetic models. If one accepts to sacrifice a full mathematical rigour, the

derivation of this expression can be short [10, 19]. Recently, another expression has been proposed [20], starting from the form that the canonical partition function assumes in mean-field-like systems; no obvious and self-evident relation with the large deviation expression can be easily found. In this work our purpose is to make a connection between these two different expressions. Our motivation is to show the equivalence of the two approaches, and at the same time to give an operative procedure for the derivation of the particular form of the canonical partition function in mean-field-like systems, that in Ref. [20] is used as a starting point, but is not derived.

In a system with N degrees of freedom and canonical coordinates $\{(q_i, p_i)\}$, we are interested in the computation of the entropy per particle in the thermodynamic limit:

$$s(\epsilon) = \lim_{N\to\infty} \frac{1}{N} \ln \int \left(\Pi_{i=1}^N \mathrm{d}q_i \mathrm{d}p_i\right) \, \delta\left(H(\{(q_i, p_i)\}) - N\epsilon\right) , \tag{1}$$

where H is the Hamiltonian and ϵ is the energy per particle (or energy density). Let us first define the class of systems that are considered here. We suppose that the Hamiltonian of our systems can be written in the form:

$$H = N \sum_{k=1}^{n} g_k(M_k), \tag{2}$$

with

$$M_k = \frac{1}{N} \sum_{i=1}^{N} f_k(q_i, p_i), \tag{3}$$

where f_k and g_k are smooth functions. It should be pointed out that the theory of large deviations can be applied to systems defined by looser conditions on the Hamiltonian; in particular, the form (2) could also be the leading term of an expansion in N, in which the relative weight of the remaining terms vanishes in the thermodynamic limit; even the simple additive structure displayed in (2) is not necessary [4]. However, for simplicity here we restrict to systems in which Eq. (2) holds exactly; moreover, we treat the case in which the $k = 1$ term is the kinetic energy, i.e., $f_1(q, p) = f_1(p) = p^2/2$ (with a suitable choice of the mass unit) and $g_1(x) = x$, while the functions f_k for $k \geq 2$ represent the interaction terms, and depend only of the configurational coordinate q. Thus, we are considering mean-field-like systems in which each particle is described by one degree of freedom. Later it will be shown that the extension to more than a degree of freedom per particle (e.g., cartesian coordinates of particles in ordinary threedimensional space) is easily performed.

We now show our first expression, that we call the large deviation expression of the entropy per particle. The cited literature can be consulted for its derivation. One finds that:

$$s(\epsilon) = \sup_{m_1,\ldots,m_n,\sum g_k(m_k)=\epsilon} J(m_1,\ldots,m_n), \tag{4}$$

where

$$J(m_1,\ldots,m_n) = \inf_{z_1,\ldots,z_n} L(z_1,\ldots,z_n,m_1,\ldots,m_n) \tag{5}$$

and where

$$L(z_1,\ldots,z_n,m_1,\ldots,m_n) = \ln\langle \mathrm{e}^{\sum_{k=1}^n z_k f_k}\rangle_1 - \left(\sum_{k=1}^n z_k m_k\right); \tag{6}$$

here $\langle\cdot\rangle_1$ is the one particle phase space (unnormalized) average defined by:

$$\langle\cdot\rangle_1 = \int \mathrm{d}q\mathrm{d}p\,(\cdot). \tag{7}$$

Of course, depending on the form of the functions f_k, there can be restrictions on the sign of the z_ks, in order to have convergence of the one particle phase space average in the right hand side of Eq. (6).

The second expression is obtained, as already mentioned, in Ref. [20], and it is derived under the hypothesis that the canonical partition function of the system can be written in the form:

$$\begin{aligned} Z(\beta) &\equiv \int \left(\Pi_{i=1}^N \mathrm{d}q_i \mathrm{d}p_i\right) \exp\left[-\beta H(\{(q_i,p_i)\})\right] \\ &= C\int \mathrm{d}y_1\ldots\mathrm{d}y_r \exp\left[N\phi(\beta,y_1,\ldots,y_r)\right], \end{aligned} \tag{8}$$

where the factor C has at most a power law dependence on N, so that it does not contribute, in the thermodynamic limit, to the free energy per particle $f(\beta)$, given by:

$$\begin{aligned} -\beta f(\beta) &= \lim_{N\to\infty}\frac{1}{N}\ln Z(\beta) \\ &= \sup_{y_1,\ldots,y_r} \phi(\beta,y_1,\ldots,y_r). \end{aligned} \tag{9}$$

In the derivation of the microcanonical entropy, apart from the assumption of analiticity, there is no other hypothesis about the form of the real function ϕ, about the number r of "order parameters", and about the way in which ϕ has been obtained. Actually, Ref. [20] treats the case $r = 1$, but the generalization to $r > 1$ is straightforward [21]. It can then be

shown that the microcanonical entropy per particle is given, in the thermodynamic limit, by:

$$s(\epsilon) = \sup_{y_1,\dots,y_r} \left[\inf_{\beta} \left(\beta\epsilon + \phi(\beta, y_1, \dots, y_r) \right) \right]. \tag{10}$$

In Ref. [20] the systems for which Eq. (8) holds are called mean-field-like systems; thus we will call Eq. (10) the mean-field-like expression of the entropy per particle. Our purpose here is to show that this last expression is equivalent to Eqs. (4-6).

First of all, let us specialize the expressions to our case, that is concerned with the most usual situation in which in the Hamiltonian there is a kinetic energy term plus terms depending only on the configurational coordinates and giving the interaction. Then, in the one particle phase space average of Eq. (6), the integrals in q and p separate; besides, the minimization problem defined in Eq. (5) decouples in one concerning z_1, that is easily solved, and one concerning $z_2, \dots, z_n$. One ends up with:

$$\begin{aligned} J(m_1, \dots, m_n) \quad &= \frac{1}{2}\ln(2\pi \mathrm{e}) + \frac{1}{2}\ln(2m_1) \\ + \inf_{z_2,\dots,z_n} \quad &G(z_2, \dots, z_n, m_2, \dots, m_n), \end{aligned} \tag{11}$$

where

$$\begin{aligned} &G(z_2, \dots, z_n, m_2, \dots, m_n) \equiv G(\{z_k\}, \{m_k\}) \\ = \; &\ln\langle \mathrm{e}^{\sum_{k=2}^{n} z_k f_k} \rangle_{1q} - \left(\sum_{k=2}^{n} z_k m_k \right), \end{aligned} \tag{12}$$

where now $\langle \cdot \rangle_{1q}$ is the analogous of Eq. (7), but with the integration only in q. Let us denote with $\overline{z}_k$, $k = 2, \dots, n$, the solution of the minimization problem defined in the right hand side of Eq. (11); the $\overline{z}_k$s are thus functions of $m_2, \dots, m_n$. Furthermore, since $g_1(x) = x$ in Eq. (2), the maximation problem in Eq. (4) can be performed by a free maximation over $m_2, \dots, m_n$ after putting:

$$m_1 = \epsilon - \sum_{k=2}^{n} g_k(m_k). \tag{13}$$

Therefore, neglecting the constant term in the right hand side of Eq. (11), we obtain:

$$\begin{aligned} s(\epsilon) = \sup_{m_2,\dots,m_n} \quad &\left[\frac{1}{2}\ln\left(2\epsilon - 2\sum_{k=2}^{n} g_k(m_k) \right) \right. \\ + \quad &\left. G(\overline{z}_2, \dots, \overline{z}_n, m_2, \dots, m_n) \right]. \end{aligned} \tag{14}$$

This is the large deviation expression of the thermodynamic limit of the entropy per particle, for the class of systems considered here.

We can now show, starting from the definition of the canonical partition function, that Eq. (10) can be transformed in Eq. (14); moreover, we can derive a definite form of ϕ in Eq. (8). In the computation of the canonical partition function, it is possible to adopt a procedure that is similar to that employed in the derivation of the large deviation expression of the entropy [19]. In fact, taking into account the form of the Hamiltonian, Eqs. (2) and (3), and specializing to our case, we can write:

$$\begin{aligned} Z(\beta) = \left(\frac{2\pi}{\beta}\right)^{\frac{N}{2}} \int \mathrm{d}q_1 \ldots \mathrm{d}q_N \mathrm{d}m_2 \ldots \mathrm{d}m_n \\ \left(\Pi_{k=2}^{n} N\delta(NM_k(\{q_i\}) - Nm_k)\right) \exp\left[-N\beta \sum_{k=2}^{n} g(m_k)\right]. \end{aligned} \tag{15}$$

The phase space coordinates are now only in the δ functions. Using the inverse Laplace transform for these functions we find that:

$$\begin{aligned} &\int \mathrm{d}q_1 \ldots \mathrm{d}q_N \left(\Pi_{k=2}^{n} N\delta(NM_k(\{q_i\}) - Nm_k)\right) \\ &= \int_{\mathcal{C}} \mathrm{d}z_2 \ldots \mathrm{d}z_n \left(\frac{N}{2\pi\mathrm{i}}\right)^n \exp\left[NG(\{z_k\},\{m_k\})\right], \end{aligned} \tag{16}$$

with the function G defined in (12), and where the integration path for each of the variables z_k is the imaginary axis, or a path obtained by deformation of the imaginary axis without crossing singularities. We compute the integral in the right hand side of (16), for $N \to \infty$, with the saddle point method (full mathematical rigour would require to prove the analiticity of the function G). To avoid unphysical oscillatory behavior, the relevant stationary point must lie on the real z_k axes. It can then be inferred that this stationary point can be found looking for the minimum of G with respect to real values of $z_2, \ldots, z_n$. This can be deduced in the following way. Let us first define the weighted one particle average $\langle \cdot \rangle_w$ by:

$$\langle \cdot \rangle_w = \frac{\langle (\cdot) \mathrm{e}^{\sum_{k=2}^{n} z_k f_k} \rangle_{1q}}{\langle \mathrm{e}^{\sum_{k=2}^{n} z_k f_k} \rangle_{1q}}. \tag{17}$$

The leading order variation ΔG around a stationary point of the function G is easily found, from Eq. (12), to be:

$$\begin{aligned} \Delta G &= \sum_{k=2}^{n} \sum_{l=2}^{n} \langle (f_k - \langle f_k \rangle_w)(f_l - \langle f_l \rangle_w) \rangle_w \mathrm{d}z_k \mathrm{d}z_l \\ &= \langle \left(\sum_{k=2}^{n} (f_k - \langle f_k \rangle_w) \mathrm{d}z_k \right)^2 \rangle_w. \end{aligned} \tag{18}$$

Restricting to real z_ks we have both that G is a real function, and that Eq. (18) is a positive quantity, meaning that a stationary point is a minimum. Thus the saddle point evaluation of the integral in the right hand side of Eq. (16) is obtained traversing the relevant stationary point along a line parallel to the imaginary axis for each z_k, so that the real part of G attains the maximum in the integration domain. At the end, keeping only the exponential dependence on N, Eq. (16) becomes:

$$\begin{aligned} &\int \mathrm{d}q_1 \dots \mathrm{d}q_N \left(\Pi_{k=2}^{n} N\delta(NM_k(\{q_i\}) - Nm_k) \right) \\ \propto\ &\exp\left[NG(\overline{z}_2, \dots, \overline{z}_n, m_2, \dots, m_n) \right]. \end{aligned} \tag{19}$$

This result can be inserted in Eq. (15), and one therefore obtains an expression like in Eq. (8), with $r = n - 1$ and, after the change of notation $y_1, \dots, y_r \to m_2, \dots, m_n$, with ϕ given by:

$$\begin{aligned} \phi(\beta, m_2, \dots, m_n) \ &= \ \frac{1}{2} \ln \left(\frac{2\pi}{\beta} \right) - \beta \sum_{k=2}^{n} g(m_k) \\ &+ \ G(\overline{z}_2, \dots, \overline{z}_n, m_2, \dots, m_n). \end{aligned} \tag{20}$$

At this point, with the very simple dependence on β of this expression, it is straightforward to perform the minimization problem in β indicated in Eq. (10); we obtain:

$$\frac{1}{\beta} = 2\epsilon - 2 \sum_{k=2}^{n} g(m_k). \tag{21}$$

This is substituted in $\beta\epsilon + \phi(\beta, m_2, \dots, m_n)$, and then the mean-field-like expression of the microcanonical entropy per particle, Eq. (10), becomes, again neglecting the same constant term as before, exactly the same as the large deviation expression, Eq. (14).

The extension to systems in which the particles move in a D-dimensional space is straightforward. In this case the canonical coordinates $\{q_i, p_i\}$ in Eqs. (1), (3), and (8) are to be intended as D-dimensional vectors $\{\mathbf{q}_i, \mathbf{p}_i\}$. Analogous replacements have to be done for the configurational coordinates q_i in Eq. (16), in the one particle phase space average $\langle \cdot \rangle_1$ (see Eq. (7)), and in its configurational restriction $\langle \cdot \rangle_{1q}$. With ϵ we still denote the energy per particle (not per degree of freedom). At the end, the common result for the large deviation and the mean-field-like expressions of the entropy per particle, Eq. (14), is simply

generalized, neglecting constant terms, to:

$$s(\epsilon) = \sup_{m_2,\ldots,m_n} \left[\frac{D}{2} \ln \left(2\epsilon - 2\sum_{k=2}^{n} g_k(m_k) \right) \right.$$
$$\left. + \quad G(\overline{z}_2,\ldots,\overline{z}_n, m_2,\ldots,m_n) \right]; \qquad (22)$$

We end with the following observation. The form obtained for the function ϕ in Eq. (20) is useful for our proof of equivalence of the two approaches to the computation of the microcanonical entropy per particle, but by no means it is unique. For example, with simple quadratic functions g_k in Eq. (2), it is common to employ the Hubbard-Stratonovich transformation [22] to linearize the dependence of the Hamiltonian on the phase space variables. One then arrives, for the canonical partition function, to an expression as in the righmost hand side of Eq. (8), with the functional form of ϕ, and the physical meaning of the "order parameters" m_k, that can be different from that in Eq. (20). Depending on the concrete cases, the function ϕ obtained may result in an expression that is easier to analyze numerically than Eq. (20).

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